(HYDRO) GASIFICATION OF BATTELLE TREATED COAL (BTC)

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INTRODUCTION

Conversion of coal to SNG is one of the options available for alleviating the critical supply shortage of natural gas. This gas supply problem is most extreme in our eastern industrial areas. However, the only commercial SNG plants using coal as a feed stock proposed thus far have been planned for the western states. A primary reason for using western coal is that the only commercially available technology that is being considered for SNG is Lurgi technology which works best with the western noncaking coals . Rapid expansion of a coal-based SNG industry in the west is limited by factors other than finding cooperative coal. For example, the issues of reclaimation of strip-mined land in arid regions, potential water supply problems, as well as the reluctance of the residents to have these areas undergo rapid industrialization can be expected to have a retarding effect on the construction of coal-conversion plants.

Availability of water, large reserves of high-sulfur coals which cannot be burned without exceeding allowable SO_2 emission levels, proximity to areas where gas shortages are most severe, the availability of an existing industrial and mining base and adequate rainfall to insure reclaimation of strip-mined land are all factors that should encourage the utilization of eastern coals as SNG feedstocks. However, the utilization of eastern coals is complicated by it's highly agglomerating nature.

Another constraint on the development of an SNG from coal industry whether it is located East or West is the capital required to build these plants. Recent estimates place the investment required for building a plant that will produce approximately 280 x 10^6 SCF/day of pipeline gas from coal in the neighborhood of $800 million.

Thus, there is a strong driving force to develop technology that will allow both the economic solution to the agglomeration problems that complicate the utilization of eastern coal and that allows the investment required to build these plants to be reduced.

One approach to lowering investment costs is by catalysis of the coal-steam-hydrogen reactions to allow the coal-steam reaction to occur at lower temperatures and the coal-hydrogen reaction at lower pressures. Numerous attempts have been made since the beginning of this century to catalyze the reaction of coal and other carbonaceous matter with steam (1-9). A few attempts have been made recently to catalyze the reaction of coal and other carbonaceous matter with hydrogen--called hydrogasification (8-12). However, it is of considerable importance to develop even better catalyst systems to promote both the hydrogasification and the steam-carbon reactions.

In this paper, we discuss the preliminary results of a novel treatment process that, in addition to enhancing the reactivity of coal to steam and hydrogen, eliminates the swelling and caking properties of even the most highly caking Eastern U.S. coals.

PROCESS DESCRIPTION

Battelle's process involves the chemical and physical incorporation of a suitable catalyst in coal.* This process is the outgrowth of a development effort to reduce the sulfur content of coal by chemical extraction that has been supported by the Battelle Energy Program. Gasification tests of the BTC showed that it had a reactivity far greater than that predictable from the results of ongoing investigations described in the literature. In addition, BTC was found to be nonswelling and noncaking. Because of these promising results, a separate effort was undertaken to develop gasification concepts and to conduct experimental feasibility studies to establish the technical and economic feasibility of this approach for the production of SNG. The results of this study have exceeded our expectations and, we believe, provide the basis for a breakthrough in SNG technology.

The catalyst usually consists of a conventional gasification catalyst and a reagent that reacts with coal to alter and open up the structure of coal facilitating the penetration of the catalyst throughout the volume of coal. During the treatment, a significant amount of catalyst (normally 1 to 3 weight percent) chemically binds to the coal while a controlled quantity of catalyst is physically incorporated into the coal. The reagent used to alter the structure of coal can be reclaimed by washing of treated coal.

EXPERIMENTAL RESULTS

A large number of gasification experiments were conducted with hydrogen and steam to determine the effects of catalyst incorporation, using the Battelle process, on the reactivity and caking properties of coal, on the gas analysis, and on the physical and chemical characteristics of the char.

Most of the experiments were conducted on 70 percent minus 200 U.S. mesh coal from the Eastern United States, containing about 30 percent volatile matter. The process was found to be applicable to coarser coals, e.g., plus 25 U.S. mesh, also. In this paper, we discuss the results with lime (CaO) as a gasification catalyst using coal from the Montour mine (Pittsburgh Seam No. 8) sized to 70 percent minus 200 U.S. mesh. The reagent and the conditions for treatment will be disclosed at a later date*. The BTC was washed prior to gasification to remove the reagent used during treatment.

The experiments were conducted in a thermobalance reactor, designed for high-pressure (1500 psig) and high-temperature (1200°C) operation, shown schematically in Figure 1. The reactor system is very similar to the one described by Gardner, et al (9). The use of the thermobalance reactor allows the monitoring of the mass of a sample as a function of time during reaction. In this manner, precise differential rate data can be obtained. The catalyst-impregnated coal was formed into 3/16-inch-diameter by 1/16-inch-long cylindrical pellets, without using a binder, since the sample container was made of 100-mesh stainless steel screen. During a run, a 2-gram sample of coal was lowered into the preheated reactor zone from the loading zone in a few seconds using a motor-operated windlass. Thus, the reaction time was precisely known. The gasification system included a steam condenser, a water trap, flowmeters, a methane-analyzer (IR), and a gas chromatograph (GC).

Prevention of Caking and Swelling

The Battelle treatment makes even the highly caking coals, e.g., coals with a free swelling index (FSI) greater than 6, completely noncaking. Figure 2 is a photograph comparing the swelling and caking of BTC with both raw coal and coal

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* Coal treated by the Battelle process is abbreviated in this paper as BTC. This process is described more fully in another paper titled "The Battelle Hydrothermal Coal Process" to be presented by E. P. Stambaugh at the 80th AIChE Meeting.

treated by impregnating it with CaO as is conventionally done. As can be seen, BTC containing 7.5 percent calcium (some of which was present as an oxide with the rest chemically bound to coal) did not swell, cake, or fuse together during hydrogasification or steam gasification while the conventionally-impregnated coal containing 14.5 weight percent calcium (20.3 percent CaO) swelled, caked, and severely fused together on steam gasification. The swelling and agglomeration of the conventionally-treated coal would have been even more extreme under hydrogasification conditions. The scanning electron micrographs of raw coal and BTC coal before and after gasification are compared in Figure 3. It can be seen that BTC does not expand or swell during hydrogasification while raw coal expands and swells severely.

The use of the Battelle process to make the coal noncaking is much more attractive than the existing state of the art which involves the preoxidation of coal or the use of rather complicated gasifiers to eliminate the need for preoxidation of coal which results in the loss of volatile matter, a reduction in the reactivity of coal, and subsequently a lowering of the efficiency of the SNG process. The Battelle process, on the other hand, involves no loss of volatile matter and substantially simpler reactor systems.

Hydrogasification Rates

The reactivities of BTC under various conditions relative to raw (untreated) coal were determined from the fractional conversion versus time data obtained from the pressurized thermobalance. The fractional conversion of coal on an ash-free basis can be defined as

$$x = 1 - \frac{(\text{mass of coal at any time}) - (\text{mass of the ash})}{(\text{initial mass of coal}) - (\text{mass of the ash})} \qquad 1)$$

For the purpose of determining the effect of Battelle treatment on the reactivity of coal, relative to raw coal, one can define an average relative reactivity, R_x, for a given fractional conversion, x, as

$$R_x = \frac{t_{x},\ \text{raw}}{t_{x},\ \text{BTC}} \qquad 2)$$

where t_{x},raw, and $t_{x,\ \text{BTC}}$ are the time required for a fractional conversion, x, of raw and Battelle-treated coal, respectively.

BTC was found to have a much higher hydrogasification reactivity than raw coal. The data in Figure 4 show that the average rate of gasification at 850°C and 500 psig hydrogen pressure based on 70 percent conversion (moisture-free basis) of BTC containing 7.5 weight percent calcium, was about 40 times faster than the raw coal.

The BTC was found to be more than an order of magnitude more reactive than coal that was impregnated with catalyst by the conventional slurry mixing at room temperature, as shown in Figure 5.

The importance of the increased hydrogasification reactivity is that high concentrations of methane should be achievable in the raw product gas thereby reducing the amount of methane that has to be produced by methanation.

One of the most important results of this work from a process economics point of view is the reduced pressure at which the BTC can be hydrogasified compared to raw coal. Figure 4 shows that even at pressures of 150 psig the BTC is much more reactive than raw coal at 500 psig. Furthermore, comparison of methane yields by graphical integration of gas analysis data (Figure 6) indicate that the methane yield, defined as the ratio of the carbon converted to methane to the total carbon gasified, of BTC at 250 psig is the same as for the raw coal at 500 psig.

Thus, because coal can be converted to methane at pressures much lower than had been previously thought possible, investment costs for SNG plants using BTC can be substantially reduced. In addition, the reliability of the plant should be significantly increased because of the lower pressure operation.

Steam Gasification Rates

Providing heat for the endothermic steam-carbon reaction is one of the factors that contributes substantially to the cost of SNG from coal. The reason for the costliness of this step is primarily that oxygen is usually used to combust part of the carbon to provide the heat. Thus, anything that can lower the temperature required for gasifying coal with steam will reduce oxygen requirements and, thereby, the SNG costs.

Experimental data show that the Battelle catalyst incorporation process allows a substantial reduction in gasification temperature over that required for either raw coal gasification or coal that contains alkali catalysts that are impregnated into the coal by conventional means. For example, Figure 7 compares the time required to achieve various gasification conversion levels for BTC, coal conventionally impregnated with CaO and raw coal all at 825°C. Clearly, the reactivity of BTC is substantially better than either of the others even though the BTC contains only about half the concentration of Ca as in the conventionally impregnated coal.

The effect of temperature on gasification rate is shown in Figure 8. Interpolation indicates that, with BTC, gasification rates at approximately 675°C are equivalent to those at 825°C with raw coal.

More important in reducing oxygen consumption than the lowering of sensible heat requirements is the higher methane yield that one expects from lower temperature operation and the catalysis of the carbon-hydrogen reaction. The higher ratio of methane to carbon oxides achievable at the lower temperature substantially reduces the endothermicity of the carbon-steam reaction.

Reactor Systems for (Hydro) Gasification)

BTC's important advantages (i.e., low temperature and pressure operability, and no swelling or caking) will have a very important impact not only on the reactor system that is developed for integration with the coal treatment step but also on other supporting operations. Obviously, BTC could be used in any of the reactor systems currently being developed. However, because of the noncaking nature of the BTC and its high reactivity a much simpler reactor system than more currently being developed for handling eastern coals should suffice.

CONCLUSIONS

The Battelle-treated coal (BTC) is a potentially superior gasification feedstock than raw (untreated) coal or coal impregnated in a conventional manner with catalysts.

The specific advantages of BTC demonstrated by this gasification study are:

1. The prevention of caking and swelling of coal during hydrogasification and steam gasification

2. High rates of steam gasification allowing steam gasification to proceed at substantially lower temperatures than with raw coal or coal treated with catalysts in a conventional manner

3. Rates of hydrogasification as high as 40 times those of raw coal and the maintenance of this high reactivity even at pressures as low as 250 psig.

Because of these advantages we believe that the development of a (hydro) gasification process based upon the use of BTC will result in a substantial lowering of both investment and operating costs as well as allow the reliable utilization of our large eastern U.S. coal reserves for the production of clean gaseous fuels.

ACKNOWLEDGMENTS

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REFERENCES

(1) Elliott, M. A., Preprints of Fuel Division, American Chemical Society Meeting, 19 (3), 140 (1974).

(2) Kroger, C., Melhorn, Gunter, Brennstoff-Chem, 19, 257 (1938).

(3) Kroger, C., Angew, Chem., 52, 129 (1939).

(4) Lewis, W. K., Gilliland, E. R., Hipkin, H., Ind. Eng. Chem., 45, 1697 (1953).

(5) Kislykh, V. I., Shishakov, N. V., Gaz. Prom., 5, 15 (1960).

(6) Willson, W. G., et al., Coal Gasification, Advances in Chemistry Series 131, Edited by L. G. Massey, American Chemical Society, Washington, D.C., 1974, p. 203.

(7) Haynes, W. P., Gasior, S. J., Forney, A. J., Coal Gasification, Advances in Chemistry Series 131, Edited by L. G. Massey, American Chemical Society, Washington, D.C., 1974, p. 179.

(8) Renwick, R. T., Wentrcek, P. R., Wise, H., Fuels, 53, 274 (October 1974).

(9) Gardner, N., Samuels, E., Wilks, K., Coal Gasification, Advances in Chemistry Series 131, Edited by L. G. Massey, American Chemical Society, Washington, D.C., 1974, p. 217.

(10) Wood, R. E., Hill, G. R., Preprints of Fuel Division, American Chemical Society Meeting, 17 (1), August, 1972.

(11) Dent, F. J., Blackburn, W. M. Millet, H. C., Trans. Inst. Gas Engrs., 87, 231 (1937).

(12) Dent, F. J., Blackburn, W. M., Millet, H. C., Inst. Gas Engrs., Commun., 190, 69 (1938).

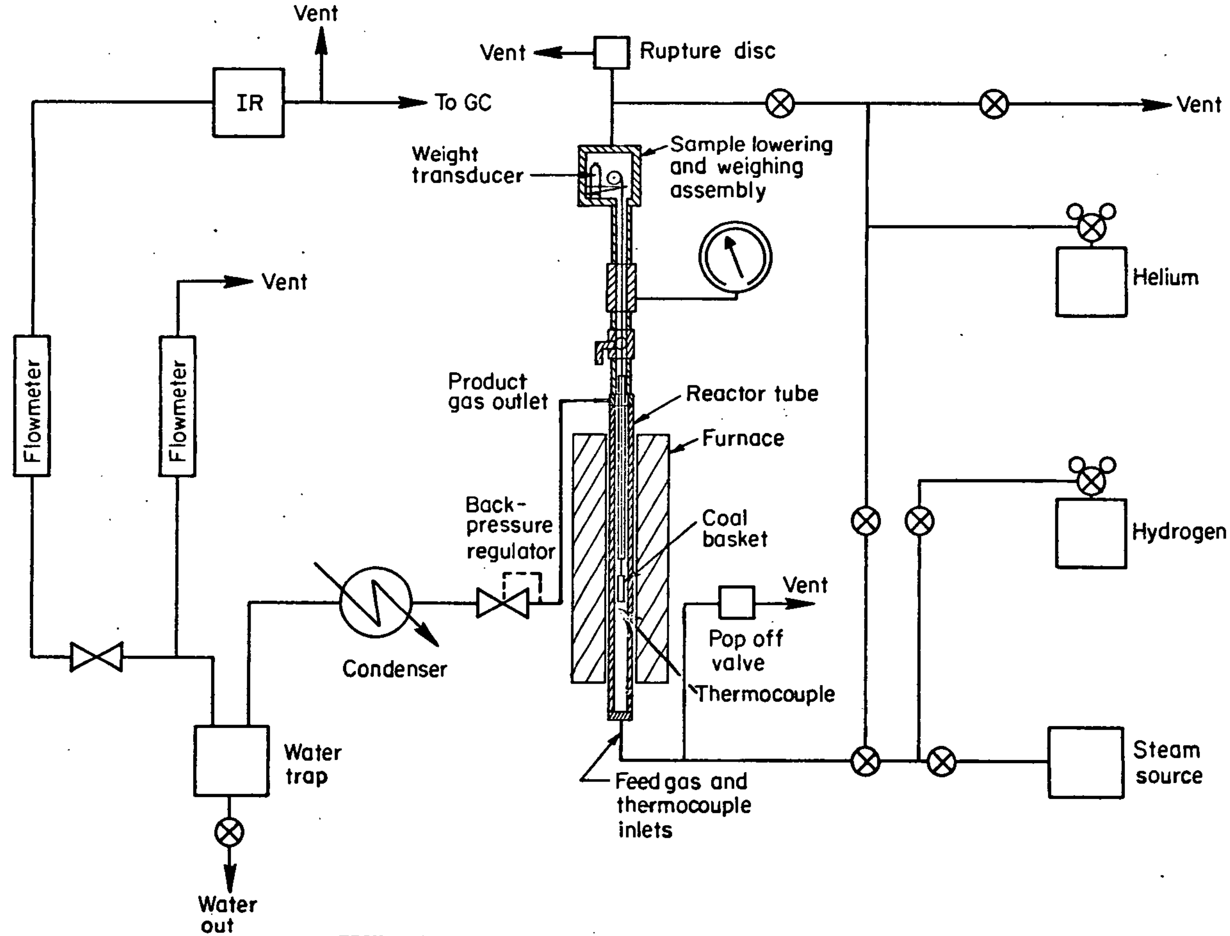


FIGURE 1. SCHEMATIC OF COAL GASIFICATION SYSTEM

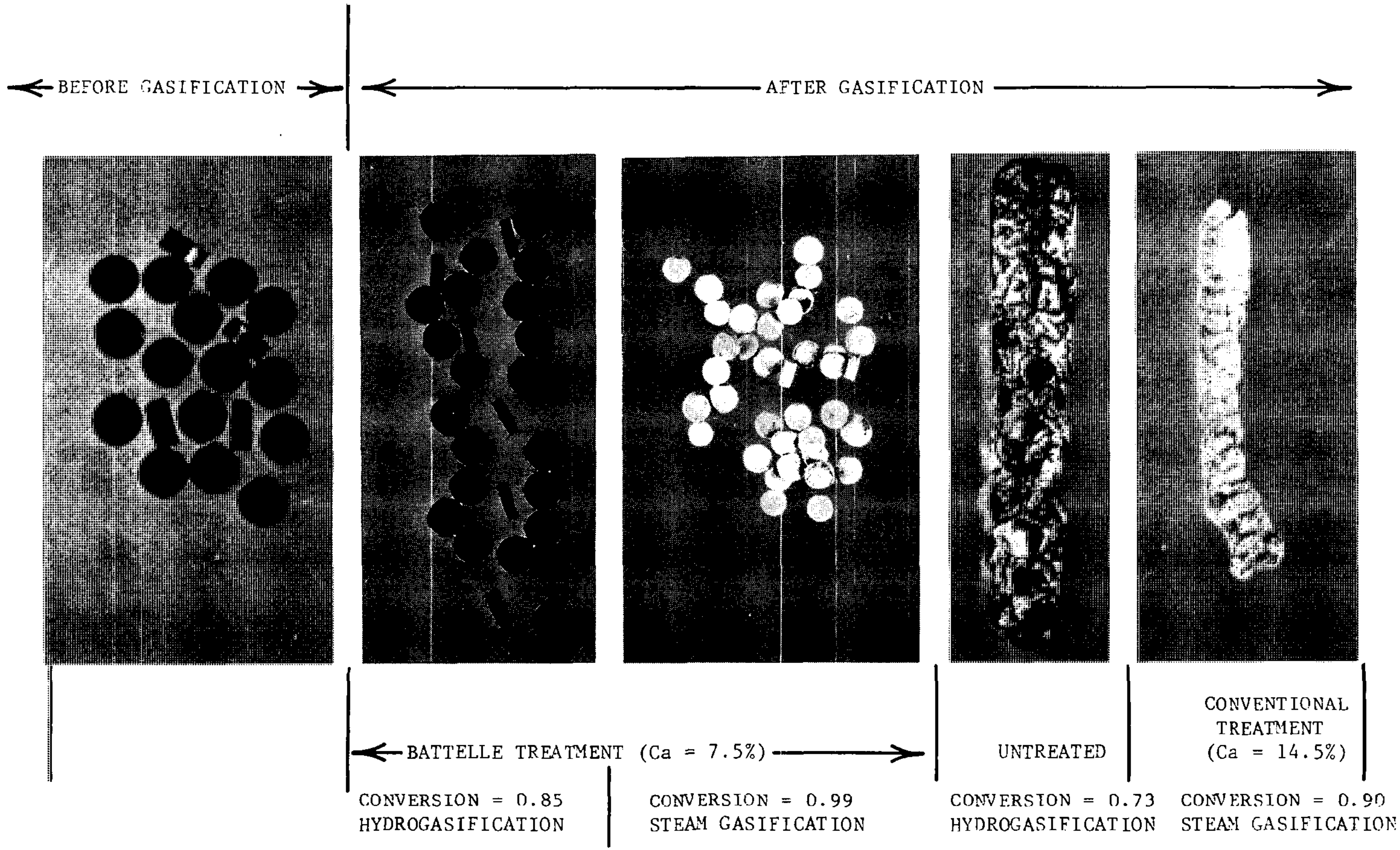
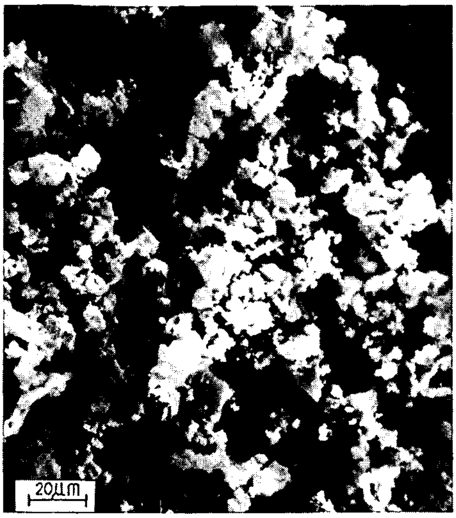
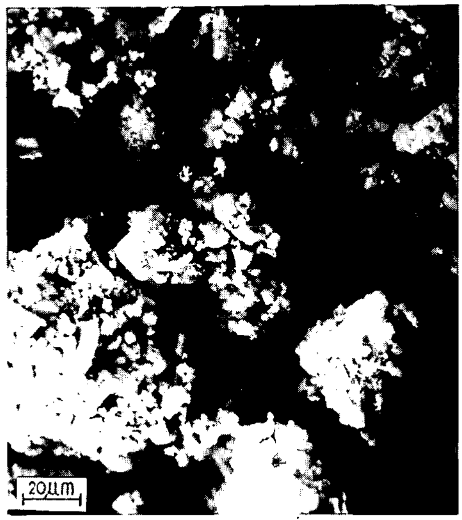


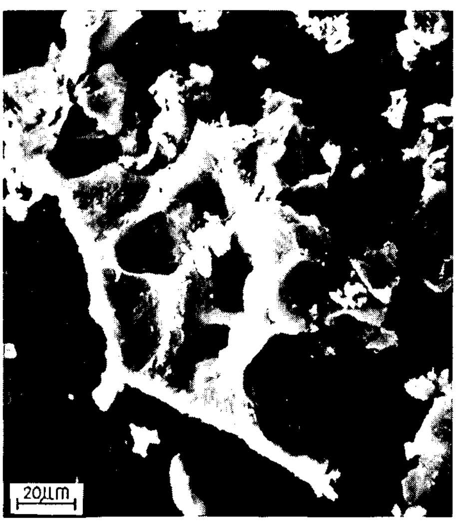
FIGURE 2. PHOTOGRAPHS OF TREATED AND UNTREATED COALS BEFORE AND AFTER GASIFICATION



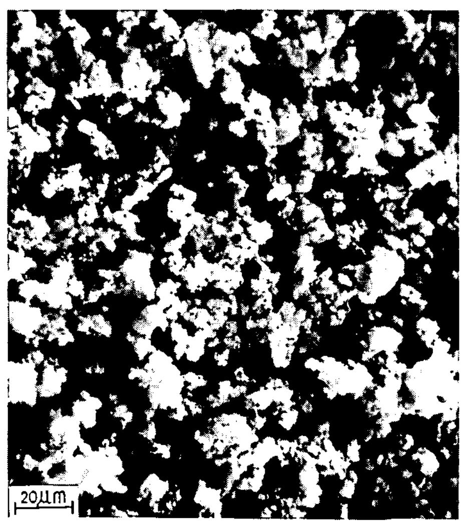
Raw Coal, Before Hydrogasification



BTC, Before Hydrogasification



Raw Coal, After Hydrogasification



BTC, After Hydrogasification

FIGURE 3. SCANNING ELECTRON MICROGRAPHS OF RAW COAL AND BTC BEFORE AND AFTER HYDROGASIFICATION

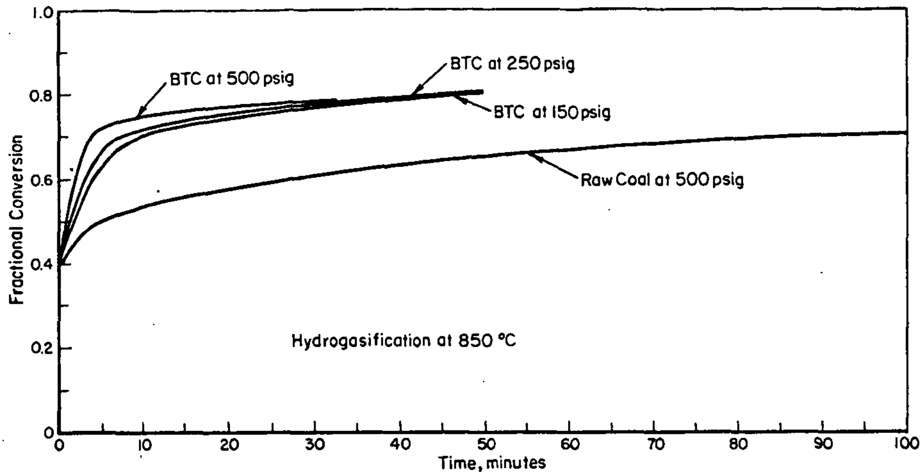


FIGURE 4. DEPENDENCE OF THE RATE OF HYDROGASIFICATION OF BTC ON PRESSURE

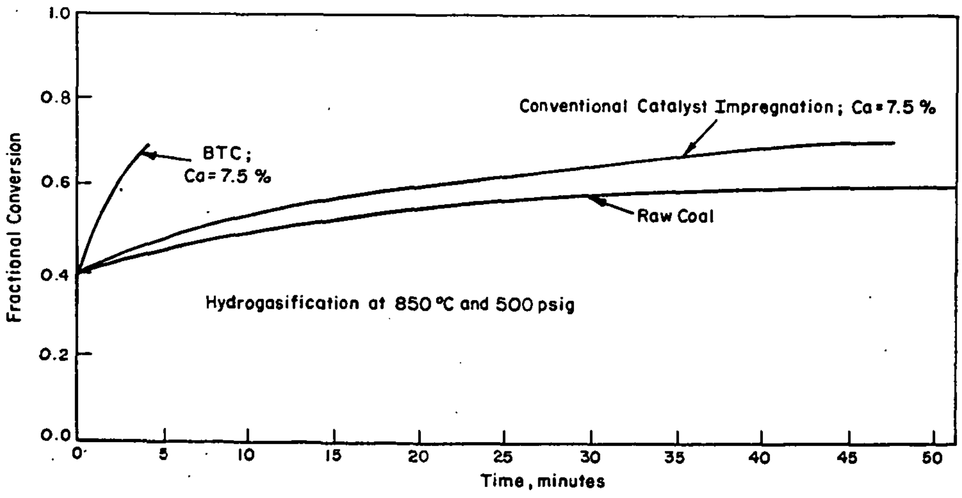


FIGURE 5. COMPARISON OF THE REACTIVITY OF BTC WITH RAW COAL AND A COAL THAT WAS CONVENTIONALLY IMPREGNATED WITH CATALYST

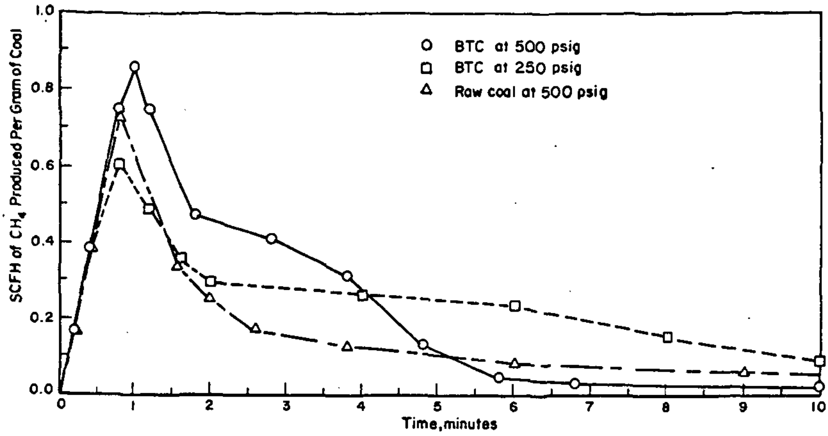


FIGURE 6. RATE OF METHANE PRODUCTION DURING HYDROGASIFICATION AT 850°C FOR COAL WEIGHING ONE GRAM (ASH-FREE) BEFORE GASIFICATION

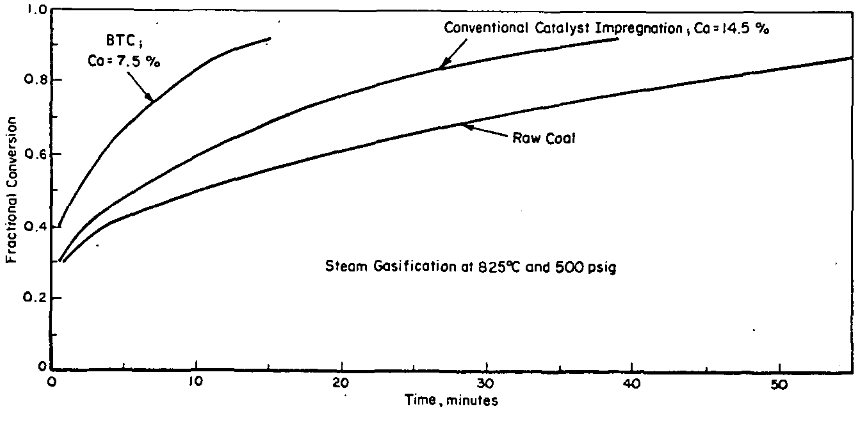


FIGURE 7. COMPARISON OF THE REACTIVITY OF BTC WITH RAW COAL AND A COAL THAT WAS CONVENTIONALLY IMPREGNATED WITH CATALYST

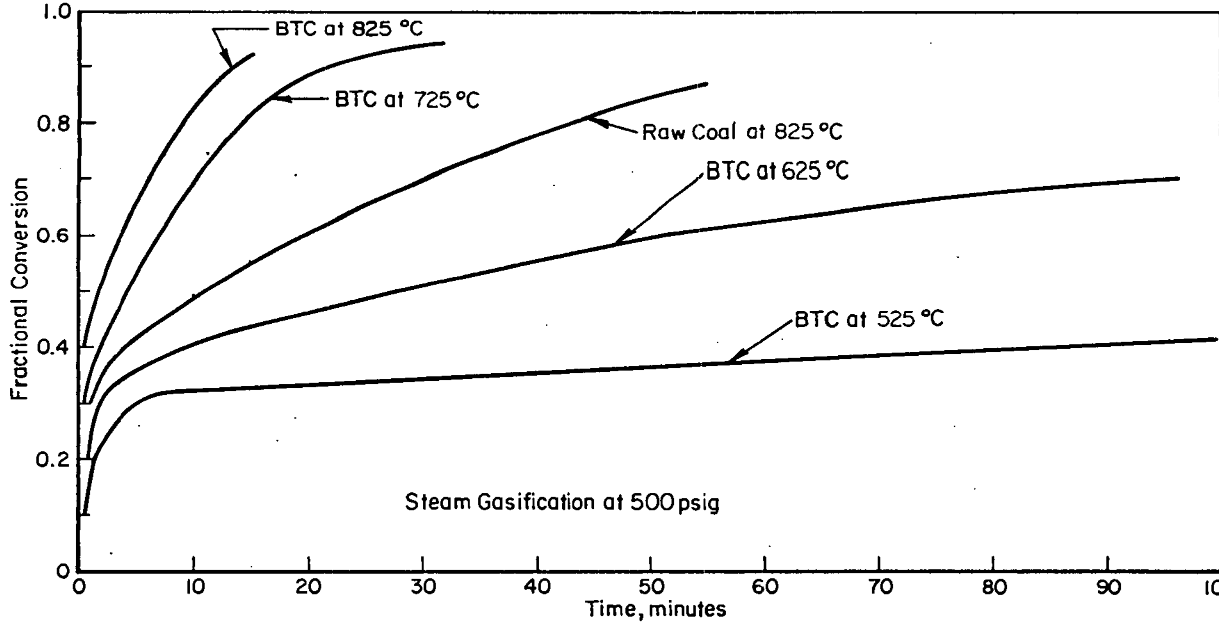


FIGURE 8. DEPENDENCE OF STEAM GASIFICATION RATE ON TEMPERATURE